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TECHNICAL ASSISTANT DOCUMENT FOR THE CHEMILUMINESCENCE MEASUREMENT OF NITROGEN DIOXIDE

Environmental Monitoring and Support Laboratory
Office of Research and Development
US Environmental Protection Agency
Research triangle Park. NC 27711

TECHNICAL ASSISTANCE DOCUMENT FOR THE CHEMILUMINESCENCE MEASUREMENT OF NITROGEN DIOXIDE

BY

Elizabeth Carol Ellis
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Research Triangle Park, NC 27711

Environmental Monitoring and Support Laboratory
Office of Research and Development
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

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PREFACE

The Environmental Protection Agency has replaced the original reference method for nitrogen dioxide with automated reference methods based on the gas phase chemiluminescence measurement principle and prescribed calibration procedures. This document provides technical information and illustrative examples to aid in the understanding of the measurement principle and particularly of the two specified calibration procedures. It should be used as a complement to both the regulatory specifications as well as individual analyzer instruction manuals and should serve to provide practical guidance to the analyst on the use and calibration of reference method analyzers -- the end result being NO2 measurements of quality. For easy reference, the regulatory specifications (prescribed in Title 40 of the code of Federal Regulations, Part 50, Appendix F) are included as an addendum.

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Abstract

Gas phase chemiluminescence has been designated as the reference measurement principle for the measurement of nitrogen dioxide (NO2) in the ambient atmosphere. Continuous analyzers based on this measurement principle may be calibrated with NO2 either from the gas phase titration of nitric oxide (NO) with ozone (03) or from an NO2 permeation device. This document presents pertinent technical information to aid in the understanding of the measurement principle and the prescribed calibration procedures and also includes illustrative examples on how to implement the calibration procedures. The discussion includes recommendations on how to recognize and eliminate potential errors in the individual calibration procedures as well as with the use of NO2 chemiluminescence analyzers. Suggestions on the design and construction of calibration apparatus and procedures for handling and certifying both NO and NO2 calibration standards are included also.

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Section 1

Introduction

In April 1971 the Environmental Protection Agency (EPA) promulgated national primary and secondary ambient air quality standards for six air pollutants, including nitrogen dioxide (NO_2). 1 At the same time EPA published reference methods that were to be used by EPA and by state and local air pollution agencies in measuring ambient concentrations of the six pollutants. Subsequent investigations2 convinced EPA that the reference method for NO_2 was severely deficient and the Administrator, in June 1973, announced his intention to proposed amendments to Federal regulations which would withdraw the original NO_2 reference method and designate a new one.3 Extensive laboratory and field evaluation of three manual and two automated methods for the measurement of NO_2 ensued. When those evaluations were completed, EPA proposed that the original NO_2 reference method be replaced by "automated reference methods" based on the gas phase chemiluminescence measurement principle and associated calibration procedures. In December 1976, this proposal became a Federal regulation.(4)

In accordance with EPA's Equivalency Regulations,(5) an NO_2 analyzer based on the gas phase chemiluminescence measurement principle could be designated as a "reference method" provided it is calibrated by specified procedures and also conforms to prescribed performance specifications. A description of the measurement principle, two alternative calibration procedures and NO_2 analyzer performance specifications are published in the Federal Register.(4) However, there are several aspects of the measurement principle and calibration procedures that warrant more detailed explanations than are possible in the Federal Register description. The basis for the following discussion is the results of laboratory evaluations(6) and field monitoring studies by the environmental Monitoring and support Laboratory (EMSL) of EPA. These comments are directed toward persons having a need to make NO_2 measurements with chemiluminescence analyzers and are offered primarily to assist the analyst in obtaining NO_2 measurements of quality.

Section 2

Chemiluminescence Measurement Principle

CHEMILUMlNESCENT REACTION OF NO WITH 03

In the reaction of nitric oxide (NO) with ozone (03), some of the resultant NO2 is produced in an electronically excited state; the excited NO2 immediately decays to the **ground** state or normal NO2 while emitting light in the spectral region from about 600 nm to 2400 nm with a peak at about 1200 nm. This phenomenon is known as chemiluminescence.] he intensity of the light generated in the NO-03 reaction is proportional to the reactant concentration of NO and the reaction is applicable to the direct measurement of atmospheric concentrations of NO. (7)

Atmospheric concentrations of NO2 are measured indirectly by chemiluminescence by first reducing the NO2 to NO, then reacting the resultant NO with ozone and measuring the light intensity from the reaction. (7-10) In practice, in chemiluminescence NO2 analyzers, the NO2 in a sample of air is first reduced to NO (11,12) by means of a converter; any NO, **which is normally** present in ambient air, passes through the converter unchanged causing a resultant total **NOx** concentration equal to NO + NO2. A portion of the air sample is also reacted with 03 without having passed through the converter. This latter No measurement is subtracted from the former measurement (NO + NO2) to yield the final NO2 measurement.

Since the detection of NO2 by this chemiluminescence technique is directly dependent on the analyzer's capability to reduce NO2 to NO, it is important that the conversion be essentially quantitative over a wide range of NO2 concentrations. Accordingly, the determination of the converter efficiency of an analyzer is an integral part of both calibration procedures with the additional requirement that the converter be replaced or serviced if its demonstrated efficiency should be less than 96 percent.

INTERFERENCES

The chemiluminescence detection of NO based upon the reaction of NO with 03 is not subject to interference from any of the common air pollutants such as 03, NO2, carbon monoxide, ammonia and sulfur dioxide.(7) However, some unsaturated hydrocarbons rect with 03 to luminesce in the visible region of the spectrum; a red sharp-cut optical filter is used to eliminate this possible interference by absorbent~ emissions below 600 nm.

Any compounds other than NO2 that will be converted to NO in the corlverte1- will interfere with the measurement of the NOx (NO + NO2) - and hence the NO2 - concentration. There are two basic types of converters in current use - thermal and chemical. Thermal converters, which are made of metallic materials such as stainless steel, operate at temperatures between 600 degrees and 800 degrees C and "thermally" reduce NO2, NO2., NO + ½ 02. At lower temperatures, NO2 conversion is not quantitative. Ammonia is the principal interferel1t of concern with thermal converters since ammonia is oxidized to NO above about 600 degrees C on

a variety of metallic surfaces. Ammonia is generally not an interferent with chemical converters which operate at temperatures as low as 200 degrees C and generally no higher than 400 degrees C. Chemical converters are made from a variety of materials: pure metals like molybdenum, tungsten or platinum; various alloys; spectroscopic carbon and some nonabsorptive charcoals; and carbon impregnated with various metals. Although of differing material composition chemical converters reduce NO2 to NO by forming an oxide of the converter material, e.g. C t No2 CO + NO. By the nature of the conversion process chemical converters will eventually expend themselves. This is no great disadvantage, however, since the carbon type converters are inexpensive to replace and the metal based converters are easily reactivated by exposing the converter surface to a reducing gas such as hydrogen. Although ammonia is not oxidized to No by chemical converters at normal operating temperatures, other unstable nitrogen compounds such as peroxyacetyl nitrate (PAN), some amines and certain organic nitrites and nitrates will decompose quantitatively to form NO.(13) The ambient concentration of these compounds is usually so slow in most areas of the country that this interference can be disregarded. However, when the concentrations of interferent compounds are significant relative to the No2 concentrations, the interference should be taken into account. If possible, the magnitude of the interferent compounds should be determined by an independent method and the NO 2 concentrations adjusted accordingly. Alternatively, it may be necessary to **determine the No2** concentrations by an equivalent method (5) that is not affected by the interferents of concern.

ANALYZER DESIGNS

Chemiluminescence NO2 analyzers employ one of two basic configurations for the NO and NOx measurements - dual or cyclic. In dual type analyzers, the air sample is divided at the analyzer inlet and half passes continuously through a converter to one reaction chamber while the other half passes continuously (through an equivalent converter volume) to a second reaction chamber. The NO and NOx concentrations are measured **continuously will** either a single detector time shared between the two reaction cells or a pair o-f matched detectors one for each reaction cell. In contrast, cyclic analyzers have a single reaction chamber and detector and must alternate between the NO and NOx measurements, i.e, the **air sample alternately** by-passes or passes through the converter. With this cyclic operation, NO and NOx readings are taken one after the other and short term changes in inlet concentration can lead to skewing of resultant NO2 values. This is not a serious problem provided the cyclic time is held to a minimum and any negative NO2 values are included in the data averaging process.

It should be noted that the use of an integrating volume on the intake of an analyzer to average any short term changes is discouraged since it introduces a distortion in the NO/NO2 ratio due to the perturbation of a photo stationary state between NO, 03 and NO2. This distortion develops because in the atmosphere the two reactions,

NO + 03 - NO2 + 03

And

NO2 sunlight NO + 0,

maintain an equilibrium. When there is no sunlight, such as in an integrating volume, the dissociation of

NO2 does not take place but the oxidation of NO still occurs. Thus, after a short time, the NO measured will be below the true value and NO2 will be higher than the true value.

Separate range selectors for No and NO2 are a useful feature of an analyzer especially when it is located in a geographical area where the NO concentration is high relative to the NO2 concentration. Independent zero and span controls and range selectors for NO, NO2 and NOX are often a common feature of cyclic type analyzers. For dual channel analyzers with a shared detector only one zero and one span control are provided; the NO and NOx are often a common feature of cyclic type analyzers. For dual channel analyzers with a shared detector, only one zero and one span control are provided; the NO and NOx measurements must be made on the same concentration range. The two detector design provides zero and span controls for both NO and NOx with range selectors which may or may not operate independently depending on the electronic design of the detector circuitry.

In a recent collaborative test (14) ten participants used ten chemiluminescence NO2 analyzers (both cyclic and dual channel designs representative of three manufacturers of NO2 analyzers) to monitor the same NO2 concentrations over a range of 0.03 to 0.16 ppm.* the results of the test for the particular analyzers involved indicate an average bias of -5% and a relative standard deviation in the measurements of 6% and 14% for within and between laboratory variation, respectively. A lower detectable limit of approximately 0.01 ppm (22ug/m3)** when using a 0.0 to 0.5 ppm range is also reported.

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*ppm = part per million.
** ug/m3 = microgram per cubic meter at 25 degrees C and 870 mm Hg.

Section 3

Calibration Procedures

GENERAL DESCRIPTIONS

There are two allowable NO2 calibration procedures (4) (see addendum): gas phase titration (GPT) of an NO standard with 03 to produce NO2 or alternatively the dilution of NO2 emitted from a permeation device. Both calibration procedures are applicable to many calibration ranges; for ambient air measurements the normal working range is 0.0 to 0.5 ppm NO2 or less. The particular NO2 concentrations used for calibration should cover the working range and should include values that are representative of those normally encountered at the location of interest as well as concentrations below and near the National Ambient Air Quality standard of 0.05 ppm NO2. (1)

The accuracy of the NO2 calibration is dependent on the analyzer's converter efficiency; therefore, a determination of converter efficiency is a required part of the calibration procedures. The measurement of converter efficiency required a source of NO as well as NO2. In essence, calibration consists of the following:

1. Calibration of NO and NOx responses of the analyzer using an NO standard.

2. Calibration of NO2 response with concurrent determination of converter efficiency using standard NO2 from GPT or from a permeation device.

It appears that GPT may be the preferred NO2 calibration scheme since both NO and NO2 are so readily available by this technique. On the other hand, some users may find it more convenient to couple an NO2 permeation device with an NO source rather than work with ozone titrations. Given that an NO source is required in both calibration procedures, the user has a choice of adding an ozone source or an NO2 permeation device to complete the calibration system.

One important feature of the two prescribed calibration procedures is the requirement that working calibration standards be traceable to National Bureau of Standards (NBS) Standard Reference Materials (SRM). For the GPR calibration option, commercially available mixtures (pressurized cylinders of No in N2) should be used for routine calibration but the No content of such mixtures must be periodically assayed against an NBS traceable NO in N2 or NO2 permeation device standard. It is also necessary to determine any trace NO2 that may be present in the commercial NO calibration mixtures. In the alternative calibration procedure using an NO2 permeation device plus an NO cylinder, only one of the two standards need be periodically assayed against an NBS traceable standard. The remaining standard is then periodically referenced to the first for consistency. Procedures for certifying an NO cylinder or NO2 permeation device against either an NO or NO2 NBS traceable standard are included below.

Details of some reliable analytical techniques as well as the apparatus for both calibration schemes are described in the sections below. The suggested component parts have been used extensively and have been found to perform satisfactorily; however, these suggestions in no way assert that other apparatus can not be used effectively.

ALTERNATIVE A: GAS PHASE TITRATION OF AN NO STANDARD WITH 03

This calibration technique is based upon the rapid gas phase reaction between No and 03 to produce NO2 as described in Equation 1. (6,15,16)

$$NO + O3 - NO2 + 02; k = 1.0 \times 107 \text{ liter mole } -1 \text{ sec } -1 \quad (1)$$

The quantitative nature of the reaction is used in a manner such that, once the concentration of reacted NO is known, the concentration of NO2 is determined. Ozone is added to excess NO in a dynamic calibration system, and a chemiluminescence No analyzer is used to measure changes in NO concentration. Upon the addition of 03, the decrease in NO concentration observed on the calibrated NO analyzer is equivalent to the concentration of NO2 produced. The amount of NO2 generated is varied by changing the concentration of 03 added.

Figure 1 shows the suggested placement of the component parts of a typical gas phase titration apparatus. Such systems are also available commercially. All connections between components in the system should be made with glass or Teflon or other nonreactive material. The discussion below is restricted to apparatus capable of producing sample flows between one and ten liters per minute (1/min) at the manifold. This is the flow range over which gas phase titration of excess No with 03 has been most widely used and investigated.

Preliminary GPT Design Consideration

In setting up the apparatus some general considerations are important. First, determine the minimum total flow required at the sample manifold. This flow is controlled by the number and sample flow rate demand of the individual analyzers to be connected to the manifold at the same time. Allow at least 10 to 50% flow in excess of the required total flow. The operational characteristics of the ozone source delimit the maximum flow of the calibration system. One ozone source that has been used extensively for gas phase titration consists of a quartz tube fixed adjacent to a low pressure mercury vapor lamp. Ozone-free air is passed through the tube and is irradiated with 185-nm light from the mercury lamp. 17,18 The level of irradiation is controlled by an adjustable opaque sleeve that fits around the lamp. Ozone concentrations are varied by adjustment of the sleeve to expose the air in the quartz tube to

FIGURE 1 COULD NOT BE SCANNED INTO THIS DOCUMENT.

various levels of ultraviolet (UV) radiation. At a fixed temperature, pressure, air flow and level of irradiation, ozone is produced at a constant rate. A change in air flow causes an inverse change in the ozone concentration when all other variables are held constant. (17) This type of ozone source can generally supply up to 3 ppm 03 at air flows in the range of 1 to 10 l/min, depending on the size of the generator.

To determine the operational characteristics of a particular ozone generator, adjust the ozone source to near maximum irradiation then measure the 03 produced at different levels of air flow through the generator, e.g., 1 to 10 l/min. (A calibrated ozone monitor or other means of measuring 03 concentrations is necessary.) A plot of the 03 concentration versus the reciprocal air flow should be linear.

The air flow that gives the desired maximum 03 concentration, as determined by the maximum concentration of NO2 needed for calibration, represents the maximum total flow for a calibration system using the generator. Of course, lower air flows can be used to generate the required 03 concentrations by simply reducing the level of irradiation of the UV lamp. If the air flow characteristics of the ozone generator do not meet the minimum total flow requirements of the analyzer under calibration, then either the generator must be replaced or the number of analyzers to be calibrated simultaneously must be reduced.

Zero Air Source and Flow Control

Purified cylinder or compressed air is suitable for the zero air; however, if large volumes of zero air are required for the calibration or especially if continuous operation is desired, purified compressed air would be preferred. The zero air must be free of contaminants, such as NO, NO2, 03 or reactive hydrocarbons, that will cause a detectable response on the NO or NO2 analyzer or that might react with either No or NO2 in the calibration system. To meet thee specifications, the air can be purified by passing it through silica gel for drying, treating it with ozone to convert any No to NO2, and passing it through a mixture of activated charcoal (6-14 mesh) and molecular sieve (6-16 mesh, type 4A) to remove any NO2, excess 03 or hydrocarbons.

Silica gel maintains its drying efficiency until it has adsorbed 20% of its weight and it can be regenerated indefinitely at 120 degrees C. The addition of cobalt chloride to the surface of the gel provides an indicating ability; this type of gel contained in a transparent drying column is recommended. The mixture of activated charcoal and molecular sieve also has a finite absorption capability. Since it is difficult to determine when the mixutre's absorption capacity has been exceeded, it is recommended that the mixture be replaced at regular intervals - at least every three months for an absorption volume of about 100 cm2.

To control and measure the air flow to an accuracy of $\pm$ 2%, as required by the calibration procedure, the following apparatus and procedures have been used successfully. Maintain the air source at a constant pressure between about 140 and 210 kPa* (20-30 kpig**) using a single stage or two stage gas pressure regulator; general purpose gas regulators work satisfactorily. When a constant air pressure is maintained upstream, fine metering needle valves can be used to maintain constant air flows in the calibration system. Volumetric flowmeters such as rotameters are an inexpensive means of measuring and monitoring the air flows. Mass flowmeters can also be used for this purpose. Either type of flowmeter must be calibrated, the former under the actual conditions of use, against a primary standard volume meter,

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*kPa = kilopascal (pascal = 1 newton/m2).
**pig = pound per square inch gauge.

E.g. , a wet test meter, that is traceable to a primary standard meter. (Nelson (19) discusses flowmeter calibration in Chapter 3 or his book.) As depicted in Figure 1, the zero air is split into two streams to allow only a portion of the total air flow to pass through the ozone generator. (Guidelines on splitting the air stream are discussed below.) The calibration range of the flowmeters used on each stream should reflect the respective air flow through that stream.

In an alternative apparatus design, all of the zero air passes through a single flow controller and flowmeter; the stream then splits with a portion of the air passing through a capillary restrictive orifice to the entrance of the ozone generator and the remainder flowing directly to the mixing chamber. When the total air flow is held constant, the proportion of air flow through the orifice and the generator remains constant. The capillary orifice should be of the proper length and internal diameter to allow the desired portion of the total air flow to pass through the ozone generator.

NO in N2 Standard, Associated Delivery Apparatus and Handling Procedures

Pressurized cylinders of No in N2 at levels between 50 and 100 ppm are available commercially as working calibration standards. The buyer should specify that oxygen-free nitrogen be used as the diluent gas for the standard mixture to minimize the problem of NO2 formation within the cylinder. In any case, the standard NO mixture must contain no more than 1.0 ppm NO2 as impurity. Since the manufacturer's certification of the No content of NO in N2 mixtures has sometimes been found to be unreliable, the calibration procedure requires that the NO content of such mixtures be assayed initially and periodically thereafter against an NBS traceable No or NO2 standard. Traceability may be made to NO SRM 1683 or 1684 or to NO2 SRM 1629. (The certification procedure is discussed below. It is suggested that the recertification of working NO standards be done on a quarterly basis since the long term stability of NO mixtures has not been firmly established.

Special apparatus and procedures apply when handling a reactive, toxic gas like NO even at concentrations of 50 to 100 ppm. It is imperative that the integrity of the No standard be maintained when the gas is transferred from the pressurized cylinder to the reaction chamber. In addition, precautions must be taken to assure that the gas is not allowed to leak to the surroundings during the transfer. All materials and surfaces that the NO gas contacts must be clean and of an unreactive material such as glass, Teflon or stainless steel. The cleanliness of the No pressure regulator and associated gas delivery system can not be overemphasized. Some of the problems of NO2 impurity in the calibration system have been traced to the conversion of the standard NO to NO2 by oxygen or other contaminants trapped within the pressure regulator and gas delivery system rather than NO2 impurity within the standard cylinder. Small amounts of NO2 formed within the pressure regulator have been found to be especially persistent.

One useful, optional feature for the No regulator is a purge port or purge assembly accessory. With purge capabilities, the regulator as well as the delivery system can be easily evacuated or purged with an inert gas such as nitrogen after the regulator is connected to the No cylinder but before the cylinder control valve has been opened. Even if the NO regulator has no purge port., regulator and delivery system contamination can be minimized and eliminated by using the following procedure:

1. Connect the pressure regulator and delivery system to the NO cylinder and evacuate the entire system before opening the cylinder control valve.

2. Open the cylinder control valve and flush the system with No for about 15 seconds at a delivery pressure of about 415 kPa (60 pig).

3. Close the cylinder control valve and re-evacuate the system. Repeat the flushing and evacuation procedures, alternately, about five times.

When flushing is complete, reduce the delivery pressure to the normal value between 140 and 240 kPa (20 and 35 pig), close the NO flow control valve, and also close the cylinder control valve until NO is required for calibrations. The should be kept pressurized and attached to the No cylinder except when the cylinder is being transported to a different location. Any time that the pressure regulator must be removed from the No cylinder, the decontamination procedures must be repeated before reuse.

The pressure regulator for the NO cylinder must be constructed of nonreactive materials; a two stage regulator (for safety precautions as well as more accurate pressure regulation) that has internal parts and diaphragm of stainless steel and a Teflon or Kel-F seat with the capability to accurately deliver a pressure of 210 kPa (30 pig) is recommended. (NOTE: All NO cylinders require a regulator with a size 660 CGA connection fitting.) A fine metering stainless steel needle valve can be used to control the NO flow to the required accuracy of $\pm$ 2%. Since the accuracy of the No flow measurement is so important to the overall accuracy of the GPT calibration procedure, special attention and due care should be given to this measurement. The recommended procedure for measuring the No flow is to measure it directly with a soap bubble meter each time the flow requires alteration. A calibrated rotameter (19) may serve as an "in-line" monitor of the No flow, but it is not recommended for absolute measurement of the No flow. Alternatively, a calibrated mass flow meter (19) may be used to both measure and monitor the NO flow accurately.

Reaction, Mixing and Sampling Chambers

The No stream combines with the 03 stream at the exit of the ozone generator (See figure 1). Immediately upon mixing of the two gas streams, the NO-03 reaction begins and it continues to completion in the reaction chamber, provided the reaction chamber is of adequate volume. The final mixture of NO2 and excess No mixes with the bulk of the zero air flows to the manifold for sampling. Glass Kjeldahl connecting bulbs make satisfactory reaction and mixing chambers. It is important in the design of these chambers that their entrance and exit ports be located at a maximum separation so that the bulk of the chamber volume is utilized for reaction or mixing. A mixing chamber volume of approximately 150 to 250 cm3 is adequate for thorough mixing of the calibration gases and diluent air; however, the volume requirements of the reaction chamber are more critical and these will be discussed in detail below. The sample manifold may be constructed of glass or Teflon (or other nonreactive material) with enough ports to accommodate the maximum number of analyzers to be calibrated simultaneously. In addition, the manifold should have a vent of sufficient diameter to assure atmospheric pressure at the sampling ports and sufficient length to prevent ambient air from entering the manifold.

NO-NO3 Reaction Requirements and Dynamic Parameter Specification

The key to a quantitative reaction between NO and 03 in gas phase titration is to provide a reaction chamber of sufficient volume to allow the reactants to remain in close proximity for a minimum time such

that the reaction goes to completion. But how does one know when this condition has been met without performing an involved calculation of reaction times from the rate equation and the initial NO and 03 concentrations in the reaction chamber? As discussed earlier, the zero air stream is split such that only a portion of the air passes through the ozone generator, increasing the concentration of)3 at the generator exit even though the)3 mass flow is constant. Thus, locally high concentrations of 03 and NO are created in the reaction chamber, which in turn provides for quantitative reaction in a much shorter time - and therefore within a much smaller volume - that would otherwise be possible. For example, if only ten percent t of the total flow (at the manifold) is passed through the ozone generator, then the initial concentrations of No and 03 in the reaction chamber are ten times greater than what their respective concentrations would be if all of the zero air was passed through the generator; thus the NO-03 reaction time decreases by an order of magnitude. It has been determined empirically (20) that the NO-O3 reaction goes to completion (less than 1% residual 03) if the following criterion is met: The product of the concentration of No in the reaction chamber, [NO]RC, (in ppm) times the residence time of the reactants in the reaction chamber, tR, (in minutes) must be at least 2.75 ppm-minutes or greater. This product is called the dynamic parameter specification, PR. Expressed algebraically, the specified condition is:

$$[NO]RC \times tR = PR \ (\geq 2.75 \text{ ppm-min}) \qquad (2)$$

where

$$[NO]RC = [NO]STD \left(\frac{FNO}{FO + FNO}\right) \qquad (3)$$

and

$$tR = \frac{VRC}{FO + FNO} < 2 \text{ minutes} \qquad (4)$$

In above equations

[NO]STD = concentration of the undiluted No standard, ppm

VRC = volume of reaction chamber, cm3

FO = air flow through 03 generator, cm3/min

FNO = NO flow, cm3/min

FT = FO = FNO + FD = total flow at manifold, cm3/min

FD = diluent air flow, cm3/min.

Application of Dynamic Parameter Specification

As the specification is written, a wide range of combinations of reactant No concentrations and

residence times is possible, giving the analyst broad latitude in designing a GPT calibration system to meet individual requirements. For rapid calibration, it is suggested that the residence time be restricted to times shorter than 2 minutes. Now the question arises as to how the dynamic parameter specification is used in actual practice to set up a GPT dynamic calibration system. The following approach is recommended.

1. Select the total flow, FT, for the calibration system as measured at the sampling manifold, the recommended range for FT is 1000 to 10,000 cm3/min. For a particular system the minimum value for FT is determined from the sample flow requirements of the analyzer(s) under calibration with provision made for a suitable excess flow. (An excess flow of at least 10 to 50% is suggested.) The maximum value for FT is determined by the operation characteristics of the particular ozone source considering the restraints on FT, the analyst should select a suitable value for FT.

2. Select a suitable volume, VRC, for the reaction chamber. This volume will be fixed (and can be estimated) if a commercial calibration system is used. The recommended range for VRC is 100 to 500 cm3.

3. Select an NO cylinder to be used for GPT that has a nominal concentration in the range of 50 to 100 ppm NO. The exact cylinder concentration, [NO]STD, is determined by referencing the cylinder against an NBS traceable NO or NO2 standard. (This procedure is discussed below.)

4. Once FT, VRC and [NO]STD are determined, calculate the flow of NO, FNO, required to generate an NO concentration at the manifold, [NO]OUT, of 90% of the upper range limit (URL) of the NO range. For example, if the URL for NO is 0.5 ppm, then the required NO concentration is 0.45 ppm.

$$FNO = \frac{[NO]OUT \times FT}{[NO]STD} \qquad (5)$$

5. Calculate the flow required through the 03 generator, FO, which results in the product of the reactant NO concentration and the residence time being equal to 2.75, i.e., set the left hand side of Equation 2 equal to 2.75 and solve for FO using Equations 3 and 4. The resulting expression is

$$FO = \frac{[NO]STD \times FNO \times VRC}{2.75} - FNO \qquad (6)$$

NOTE: The value of FO determined by Equation 6 is the maximum value for FO. Lower values of FI may be used.

6. Calculate the diluent air flow, FC.

$$FD = FT - FO - FNO \qquad (7)$$

7. Calculate the reactant NO concentration from Equation 3.

8. Calculate the residence time in the reaction chamber from Equation 4. For a rapid calibration, the residence time should be less than 2 minutes.

9. As a final check, calculate the dynamic parameter, PR, for the reactant No concentration and the residence time as determined in steps 7 and 8 above,

$$PR = [NO]RC \times tR = [NO]STD \left(\frac{FNO}{FO + FNO}\right)\left(\frac{VRC}{FO + FNO}\right) \qquad (2')$$

Varying any single parameter on the right-hand side of Equation 2' affects PR as follows:

a. Decrease in FO - increase in PR.
b. Increase in VRC - increase in PR.
c. Increase in FNO - increase in PR.

Example. Calibrate two NO2 analyzers, each requiring a sample flow of 250 cm3/min. The calibration range for each is 0.05 ppm NO2. Set up a GPT dynamic calibration system using an available ozone generator that will produce about 0.5 ppm 03 at a total air flow of about 5 l/min.

1. Select the total flow, FT.

FT (minimum) = 2(250) + 500 (excess)
= 1000 cm3/min
FT (maximum)= 5000 cm3/min
Let FT = 3000 cm3/min.

2. Select a reaction chamber volume, VRC. A Kjeldahl connecting bulb of about 300 cm3 in volume is available.

VRC = 300 cm3.

3. An NO cylinder containing 80.0 ppm NO in N2 is available.

[NO]STD = 80.0 ppm.

4. Calculate FNO. The required NO concentration is0.45 ppm (90% of URL of 0.5 ppm).

$$FNO = \frac{[NO]OUT \times FT}{[NO]STD} = \frac{(0.45 \text{ ppm})(3000 \text{ cm3/min.})}{} = 16.9 \text{ cm3/min.}$$

5. Calculate FO.

$$FO = \frac{[NO]STD \times FNO \times VRC}{2.75} - FNO$$

$$= \frac{(80.0 \text{ ppm})(16.9 \text{ cm3/min})(300 \text{ cm3})}{2.75 \text{ ppm-min}} - 16.9 \text{ cm3/min}$$

= 384.0 cm3/min - 16.9 cm3/min

= 367 cm3/min.

6. Calculate FD.

FD = FT - FO - FNO

= (3000 - 367 - 16.9) cm3/min

= 2616 cm3/min.

7. $[NO]RC = [NO]STD \left(\frac{FNO}{FO + FNO}\right)$

$= 80.0 \text{ ppm} \frac{16.9 \text{ cm3/min}}{(367 + 16.9) \text{ cm3/min}}$

= 3.52 ppm.

8. $tR = \frac{VRC}{FO + FNO}$

$= \frac{(300 \text{ cm3})}{367 \text{ cm3/min} + 16.9 \text{ cm3/min}}$

= 0.781 min.

9. PR = [NO]RC x tR

= (3.52 ppm) (.781 min)

= 2.75 ppm-min.

A GPT system with the following operating conditions will be suitable to perform the calibration:

FT = 3000 cm3/min

VRC = 300 cm3

FNO = 16.9 cm3/min

FO = 367.1 cm3/min

FD = 2616 cm3/min.

Changes in the above conditions are possible as long as the dynamic parameter $\geq$ 2.75 is maintained.

Check for completeness of NO-O3 Reaction

After the gas phase titration apparatus has been assemble, the completeness of the NO-O3 reaction may be verified before proceeding with the calibrations. This verification must be made if the dynamic parameter for the GPT system is less than 2.75. A chemiluminescence 03 analyzer (calibrated to within $\pm$ 50%) connected to the manifold is required for this experiment. Generate an NO concentration near 90% of the upper range limit of the desired NO range; for 0 to 1.0 ppm and 0 to 0.5 ppm ranges, the required No concentration is about 0l9 and 0.45 ppm NO, respectively. Next, adjust the ozone source to generate enough 03 to produce an NO2 concentration of approximately 80% of the upper range limit of the NO2 range. For an NO2 range of 0 to 0.5 ppm, the required 03 and NO2 concentrations would be about 0.4 ppm. (The suggested upper range limit for NO2 analyzers that are calibrated for ambient air monitoring purposes is 0.5 ppm or less.) This is the most critical point in the gas phase titration since about 90% of the available NO must be reacted for the reaction to be complete. Note the response of the ozone monitor. There should be no detectable 03 response measured by the 03 analyzer if the NO-03 reaction goes to completion in the reaction chamber. An 03 response greater than 1% of the available 03 concentration indicates an incomplete NO-03 reaction.

NO2 Analyzer Calibration

Once the gas phase titration system has been assembled and is operative and the NO working standard has been certified (see the following section), the actual calibration of an NO2 chemiluminescence analyzer is straightforward. The object of the calibration is to determine the NO, NO2 and NOx responses of the analyzer as a function of known NO and NO2 concentrations. This requires that adjustments be made to the zero and span controls of the analyzer; the number and function of these controls will vary according to analyzer design. For analyzers with only one zero or span control, the respective zero or span adjustments are made with respect to the NO response of the analyzer. Once these adjustments are made the NO2 and NOX responses are then exact, or else, reduced by a factor equivalent to the converter efficiency of the analyzer. Adjustments to analyzers with two zero or two span controls are made with respect to the NO and NOX responses - both span adjustments are made using an NO source; the NO2 response is again fixed and reflects any inefficiency of the converter. Zero and span adjustments to analyzers with three separate zero or span controls must be made for all three analyzer responses - NO, NOx and NO2. For these analyzers, the NO and NOx span adjustments are made using a known No concentration and the NO2 adjustment is made using a known NO2 concentration. By adjusting the NOx span control with essentially NO only, the converter efficiency can be determined. For a particulate analyzer, the instruction manual will provide an in-depth discussion of its design and operational controls.

A brief outline of the GPT calibration procedure follows:

1. Select the analyzer calibration ranges for NO, NOX and NO2.

2. Connect strip chart recorders to the analyzer records terminals. Consult the recorder instruction manual for procedures on making zero, gain, span, damping and other operational adjustments.

3. Allow the analyzer to sample zero air. (The NO source should be vented to exhaust.) Make adjustments to the analyzer zero control(s) such that the analyzer and recorder responses are offset by + 5% of the full scale range. (For a calibration range of0 to 0.5 ppm, the zero offset would be equivalent to 0.025 ppm.)

4. Adjust the No flow to generate an NO concentration of about 80% of the upper range limit of the NO range. After the analyzer's responses stabilize, adjust the No span control such that the NO recorder response reflects the exact No concentration generated plus the No zero offset. Also, adjust the NOx span control (for analyzers equipped with two or three span controls) such that the NOx recorder response reflects the sum of the following: the NO concentration, any NO2 impurity concentration in the No working standard and the NOx zero offset. No NOx span adjustment is necessary for analyzers with only one span control.

NOTE: If the analyzer No and NOx responses fail to stabilize (all flows constant) with the NO response gradually increasing and the NOx response gradually decreasing, check for contamination of the NO pressure regulator and delivery system.

5. Generate about five additional NO concentrations over the NO/NOX range and record the analyzer NO and NOx responses (taken from the strip chart recorders) to each concentration. Plot the NO and NOx calibration curves as explained in the calibration procedure.

6. Generate an NO concentration of about 90% of the NO range. Using the NO and NOx calibration curves, measure and record the NO concentration as [NO]orig and the NOx concentration as [NOx] orig.

7. Adjust the 03 generator to generate sufficient 03 to produce an NO2 concentration of about 80% of the selected NO2 range. When the analyzer responses have stabilized, measure (from calibration curves) and record the resultant No and NOx responses as [NO]rem and [Nox]rem, respectively. No NO2 span adjustment is necessary for analyzers with one or two span controls. For analyzers with three span controls, adjust the NO2 span control so that the NO2 recorder response reflects the sum of the following: the NO2 concentration generated by GPT ([NO]orig - [NO]rem), and NO2 impurity in the No standard and the NO2 zero offset. Record the stable NO2 response.

8. Adjust the ozone generator to obtain at least five other NO2 concentrations over the NO2 range and record the analyzer's stable NO, NOx and NO2 responses (strip chart readings) to each concentration. Plot the NO2 calibration curve as explained in the calibration procedure. (4)

9. Determine the converter efficiency. The total NO2 concentration generated at the manifold [NO2]out, during the GPT is given by the sum of the NO2 concentration from GPT plus any NO2 impurity from the NO cylinder.

$$[NO2]out = ([NO]orig - [NO]rem) + NO2\ impurity. \quad (8)$$

The total NO2 concentration converted to No in the analyzer, [NO]conv, is given by

$$[NO2]conv = [NO2]out - ([Nox]orig - [Nox]rem). \quad (9)$$

The slope of a plot of [NO2] conv versus [NO2]out is the average converter efficiency of the analyzer. If the converter efficiency is less than 96%, replace or service the converter.

Certification of NO in N2 Working Standard Against NBS Traceable Standards

The NO content of the NO working standard must be periodically assayed against NBS traceable NO or NO2 standards. Any NO2 impurity in the cylinder must also be assayed. Certification of the NO working standard should be made on a quarterly basis or more frequently as required. Procedures are outlined below for certification against either an NO or NO2 NBS traceable standard. The simplest and most straightforward procedure is to certify against an NO standard. NOTE: If the assayed NO2 impurity concentration, [NO2]IMP, is greater than the 1 ppm value allowed in the calibration procedure,4 make certain that the NO delivery system is not the source of contamination before discarding the NO standard.

Certification of No Working Standard Against an NBS Traceable NO Standard

Use the NBS traceable NO standard and the GPT calibration procedure to calibrate the NO, NOx and NO2 responses of a chemiluminescence analyzer. Also determine the converter efficiency of the analyzer. Refer to the calibration procedure(4) for exact details; ignore the recommended zero offset adjustments.

Generate several No concentrations by dilution of the NO working standard. Use the nominal NO concentration, [NO]nom, to calculate the diluted concentrations. Plot the analyzer No response (in ppm) versus the nominal diluted NO concentration and determine the slope, SNOM. Calculate the No concentration of the working standard, [NO]STD, from

$$[NO]STD = [NO]NOM \times SNOM \quad (10)$$

If the nominal NO concentration of the working standard is unknown, generate several NO concentrations to give on-scale No responses. Measure and record FNO and FT for each NO concentration generated Plot the analyzer No response versus FNO/FT and determine the slope which gives [NO]STD directly.

The analyzer NOx responses to the generated NO concentrations reflect any NO2 impurity in the NO working standard. Plot the difference between the analyzer NOx and NO responses versus FNO/FT. The slope of this plot is [NO2]IMP.

In the procedure above it is possible to assay the No content of the working standard without first calibrating the No and NOx responses of the analyzer. This is done by simply comparing relative NO responses of the working NO standard to the NBS traceable No standard. The NO2 impurity can be determined from the analyzer NOx responses provided the converter efficiency is known.

Certification of NO Working Standard Against an NBS Traceable NO2 Standard.

Use the No working standard and the GPT calibration procedure to “calibrate” the NO, NOx and

NO2 responses of a chemiluminescence analyzer. Refer to the calibration procedure (4) for exact details; ignore the recommended zero offset adjustments. For this pseudo-calibration use the nominal NO cylinder value and assume no NO2 impurity is in the cylinder. For an analyzer with dual detectors the NOx span adjustment must be made by diverting the sample flow around the converter and routing it directly to the NOx detector. This operation electronically balances the two detectors.

From the GPT data, plot the analyzer NO2 response versus the NO2 concentration generated by GPT. Determine the slope, SNOM, and the X-intercept of the curve. Generate several NO2 concentrations by dilution of the NBS traceable NO2 standard. Plot the analyzer NO2 response versus NO2 concentration. Determine the slope, SNBS. Calculate the NO concentration of the working standard, [NO]STD, from

$$[NO]STD = [NO]NOM \times \frac{SNOM}{SNBS} \qquad (11)$$

Calculate the NO2 impurity from

$$[NO2]IMP = \frac{(X\text{-intercept})\ FT}{FNO} \times \frac{SNOM}{SNBS} \qquad (12)$$

ALTERNATIVE B: NO2 PERMEATION DEVICE

In a permeation device, (21) an easily liquefiable gas such as NO2 is condensed inside an inert container, all or part of which is constructed from a polymeric material (often Teflon). Gas escapes from the container by dissolving in and permeating through the polymer walls at a temperature dependent rate. The rate of gas effusion (in ug/min) at a constant temperature can be established by gravimetric determination of the weight loss of the permeation device over a known period of time. In this calibration procedure, the NO and NOx responses of a chemiluminescence analyzer are first calibrated with an NO standard; next accurately known concentrations of NO2 are produced dynamically by diluting the effusion from an NO2 permeation device with various flows of clean air to obtain a calibration for NO2. Either the NO2 permeation device or the No source may be chosen as the reference standard for calibration. The remaining standard must be assayed against the reference standard for consistency.

Components of a Permeation Device Calibration System

Figure 2 shows a diagram of a typical permeation device calibration system. Such systems have been described in the literature (21,22) and they are also commercially available. All connections between components in the system should be glass or Teflon or other nonreactive material. The system consists of four functional sections:

1. A controlled-temperature section that houses the NO2 permeation device and is flushed continuously with purified, dry zero air or nitrogen.

2. A regulated of clean, dry zero air fro dilution of the NO2 gas effluent from the permeation device. The source should be capable of providing air flows up to about 20 1/min.

3. An NO standard and delivery system.

4. A dilution-mixing, sampling and exhaust section.

The suggestions for preparing, regulation and measuring zero air flows discussed in connection with gas phase titration are applicable to this calibration system also. In addition, an NO standard with delivery system and a suitable dilution-mixing, sampling and exhaust assembly were also discussed above. Therefore, the latter three sections of the permeation device calibration system do not warrant further discussion. A description of the constant temperature section follows:

Constant Temperature Section

Temperature control is the primary concern in using an NO2 permeation device as a standard NO2 source. For example, a change in temperature of about 0.5 degrees C effects a change in the permeation rate of the device of about four percent (4%) . For this reason, it is important that the temperature of the device be maintained at a constant value within ±0.1 degrees C and that it be closely monitored when the device is in use.

Generally, the NO2 permeation device is housed in a temperature-controlled glass container that has an entrance and exit port at opposite ends; a glass thermometer accurate to ± 0.05 degrees C may be placed beside the device to monitor its temperature. A small fixed zero air or nitrogen flow (about 100 cm3/min) that is maintained at the same temperature as the permeation device flushes the NO2 out of the device housing into a mixing chamber where the NO2 is diluted with clean dry zero air. A valve, e.g., a three-way stop clock, placed at the exit of the device housing may be used to divert the NO2 stream to a vent when clean air is required at the manifold for making the necessary zero adjustments to the analyzer.

To maintain the temperature of the permeation device to within ± 0.1 degree C of the desired

FIGURE 2 COULD NOT BE SCANNED INTO THIS DOCUMENT.

Value, the device and housing may be either placed physically inside a constant temperature chamber as depicted in Figure 2 or they can e located external to the constant temperature chamber with the heat transfer medium circulated around the device housing, e.g., a jacketed condenser (West or Liebig type). The flushing zero air or nitrogen passes through a heat exchanger, e.g., a coil of copper tubing, contained in the constant temperature chamber before passing over the device to adjust its temperature to that of the device. For a calibration system to be used in a laboratory or other permanent location, a circulating water bath makes an excellent constant temperature chamber. Many circulating water baths are available that are capable of temperature control to ± 0.1 degree C over a suitable temperature range (usually 15 degrees C to 35 degrees C for most calibration work). Commercial calibration systems often use circulating air in the constant temperature chamber; such a chamber has the advantage of being more portable than a water bath.

Flush Gas for Permeation Device. In Figure 2 the zero air stream is split to allow a small air flow to pass continuously over the permeation device. Alternatively, the flush gas could be supplied from a cylinder of prepurified dry air or nitrogen. Whatever its source is extremely important that the flushing stream be

extra dry so that moisture does not condense on the surface of the device. Water condensate could react with the effusing NO2 to form an acid mist thus changing the NO2 concentration. A transparent drying column containing a mixture of molecular sieve (e.g., 6-16 mesh, type 4A) and indicating calcium sulfate (e.g., Drierite) has been used effectively as a moisture scrubber on the flush gas line.

Standard NO2 Permeation Device

The diffusion properties of NO2 has made the construction of stable, accurate NO2 permeation devices no each feat. For this reason due care must be given to their handling for reliable use. Permeation devices are available from commercial sources and from NBS as a Standard Reference Material (SRM 1629). The NBS device has a certified permeation rate of approximately 1 ug/min at about 25 degrees C. Permeation rates of commercial devices vary according to size and recommended operating temperature. Both NBS and commercial manufacturers provide explicit instructions on the use of their respective devices which the user should follow for accurate measurements.

Most permeation devices must equilibrate for at least 24 hours at the certified or operating temperature before the permeation rate stabilizes. Equilibration times may be longer and the permeation rate may be erratic if the device is subjected to extreme temperature variations when not in use. It was mentioned above that the flush gas over the permeation device must be extra dry. This is especially true of the NBS device and many others which have a large surface area for NO2 permeation. Some commercial devices which have a very small permeating area and are designed to operate at elevated temperatures (40 to 60 degrees C) may not be as susceptible to trace moisture in the flush gas. Additional information regarding the use of permeation devices for calibration purposes is documented elsewhere. (22-24)

If the NO2 permeation device is to be used as the reference standard for calibration, then the permeation rate of the device must be traceable to an NBS NO in N2 standard (SRM 1683 or 1684)or NO2 standard (SRM 1692). Otherwise, the permeation device need only be periodically assayed against the reference NO standard to assure consistency between the two working standards. Procedures for certifying the reference standard against NBS traceable NO2 or NO in N2 standards and for intercomparing the NO2 and NO working standards are discussed below.

Basic Design Considerations for a Calibration System

When designing a calibration system, the analyst should first determine the relevant operational criteria that the system must meet. The calibration range(s) that the system must accommodate should be considered along with the corresponding total air flow that will be required for maximum flexibility, the system should be designed for use with the widest applicable range (normally 0 o 0.5 ppm NO2 for ambient air measurements); it will serve more sensitive ranges when necessary. Since the NO2 concentration is inversely proportional to the total flow at the manifold, the minimum required NO2 concentration sets the upper limit of the dilution air flow. For example, using one NBS permeation device that generates about 1 ug NO2/min, a total air flow of about 18 l/min is required to generate about 0.03 ppm NO2. Lower concentrations would, of course, require higher dilution air flows. A second consideration is the number of NO2 analyzers that can be calibrated simultaneously with the calibration system. This is controlled not only by the sum of the respective analyzer sample flow rates but also and most importantly, by the minimum total flow of the calibration system at the manifold. Air flow is a

minimum when the NO2 concentration is a maximum. As specified in the calibration procedure, the maximum required NO2 concentration is about 80% of the calibration range. For example, again using one NBS permeation device and specifying and NO2 analyzer range of 0 to 0.5 ppm NO2, a total flow of about 1.3 l/min is required to generate about 0.4 ppm NO2. Allowing about 0.3 1/min as excess flow, only about 1.0 l/min flow is available at the manifold for calibration of the NO2 analyzer(s). If the lower limit of the total flow of the NO2 calibration gas is insufficient to meet the flow demand of the NO2 analyzer(s), then the problem could be solved by calibrating and using the analyzer(s) on a more sensitive range whenever possible and appropriate. Alternatively, two or more permeation devices could be used in parallel to generate NO2 concentrations at the upper end of the calibration range. For example, two NBS devices would permit the doubling of the total flow at the manifold. By venting the effluent of all but one of the devices, NO2 concentrations in the lower portion of the range could be easily provided.

NO2 Analyzer Calibration

Once the permeation device system has been assembled and is operative and the NO and NO2 working standards have been intercompared with respect to the certified standard (see the following section), the actual calibration of and NO2.

Chemiluminescence analyzer is straightforward. The object of the calibration is to determine the NO, NO2, and NOx responses of the analyzer as a function of Known NO and NO2 concentration This requires that adjustments be made to the zero and span controls of the analyzer; the number and function of these controls will vary according to analyzer design. For analyzers with only one zero or span control, the respective zero or span adjustments are made with respect to the NO response of the analyzer. Once these adjustments are made the NO2 and NOx responses are then exact, or else, reduced by a factor equivalent to the converter efficiency of the analyzer. Adjustments to analyzer with two zero or two span controls are made with respect to the No and NOx responses - both span adjustments are made using an NO source; the NO2 response is again fixed and reflects any inefficiency of the converter. Zero and span adjustments to analyzers with three separate zero or span controls must be made for all three analyzer responses - NO, NOx and NO2. For these analyzers, the NO and NOx span adjustments are made using a known NO concentration and the NO2 adjustment is made using a known NO2 concentration. By adjusting the NOx span control with essentially NO only, the converter efficiency can be determined. For a particular analyzer, the instruction manual will provide an in-depth discussion of its design and operational controls.

A brief outline of the calibration procedure follows:

1. Select the analyzer calibration ranges for No, NOx and NO2.

2. Connect strip chart recorders to the analyzer recorder terminals. Consult the recorder instruction manual for procedures on making zero, gain, span, damping, and other operational adjustments.

3. Allow the analyzer to sample zero air. (The NO and NO2 sources should be vented to exhaust.) Make adjustments to the analyzer zero control(s) such that the analyzer and recorder responses are offset by + 5% of the full scale range. (For a calibration range of 0to 0.5 ppm, the zero offset would be equivalent to 0.025 ppm.)

4. Adjust the NO flow to generate an NO concentration of about 80% of the upper range limit of the NO range. After the analyzer's responses stabilize, adjust the NO span control such that the No recorder response reflects the exact NO concentration generated plus the NO zero offset. Also adjust the NOx span control (for analyzers equipped with two or three span controls) such that the NOx recorder response reflects the sum of the following: the No concentration, any NO2 impurity concentration in the No working standard and the NOx zero offset. No NOx span adjustment is necessary for analyzers with only one span control.

NOTE: If the analyzer NO and NOx responses fail to stabilize (all flows constant) with the NO response gradually increasing and the NOx response gradually decreasing, check for contamination of the NO pressure regulator and delivery system.

5. Generate about five additional NO concentrations over the NO/NOX range and record the analyzer NO and NOx responses (taken from the strip chart recorders) to each concentration. Plot the No and NOx calibration curves as explained in the calibration procedure. (4)

6. Divert the NO flow to exhaust and the NO2 flow to the manifold. Adjust the dilution air flow, FD, to generate an NO2 concentration of about 80% of the upper range limit of the NO2 range. After the analyzer response stabilizer, adjust the NO2 span control (only for analyzers with three span controls) so that the NO2 recorder response reflects the sum of the NO2 concentration from the permeation device plus the NO2 zero offset. Record the stable NO2 and NOx responses.

7. Generate at least five additional NO2 concentrations by varying the dilution air flow; record the stable NO2 and NOx responses to each concentration. An equilibration time of at least ten minutes is suggested between concentration changes. Plot the NO2 calibration curve as explained in the calibration procedure.(4)

8. Determine the converter efficiency. The NO2 concentration at the manifold, [NO2] out, is calculated from the permeation rate and the total flow at the manifold. The NO2 concentration converted to No by the analyzer is given by the NOx response to the generated NO2 concentrations. The slope of a plot of the NOx response versus [NO2]out gives the average converter efficiency of the analyzer. If the converter efficiency is less than 96%, replace or service the converter.

<u>Certification of Working NO2 or NO in N2 Standard Against NBS Traceable Standard</u>

Either the NO2 permeation device or the NO source may be chosen as the reference standard for calibration. The reference standard must be certified against an NBS traceable standard. The remaining standard must then be assayed against the reference standard for consistency. To show consistency, the NO2 generated by a permeation device is compared to the NO2 generated by gas phase titration of the NO standard. Certifications and intercomparisons should be done quarterly or more frequently as required.

:[f the NO standard is chosen as the reference standard, it may be certified against an NBS traceable NO2 or NO standard. These certification procedures were outlined above under the discussion of gas phase titration and need not be repeated here. Certification of' an **NO2 standard** against NBS traceable standards and the intercomparison of the NO and NO2 standards are discussed below.

Certification of NO2 Working Standard Against an NBS Traceable NO2 Standard

The NO2 chemiluminescence analyzer need not be in calibration for these measurements. Generate several NO2 concentrations by dilution of the NBS traceable NO2 standard. Plot the analyzer NO2 response versus NO2 concentration and determine the slope, SNBS. Generate several NO2 concentrations by dilution of the working NO2 standard to give on-scale **NO2** responses. Measure the total flow at the manifold, FT, for each NO2 concentration generated. Plot the analyzer NO2 response versus 1/FT and determine the slope, SSTD. Calculate the permeation rate, R, from

$$R = \frac{SSTD}{KxSNBS} \qquad (13)$$

where

K = 0.532 ul NO2/ug NO2 (at 25 degrees C and 760 mm Hg).

Certification of NO2 Working Standard Against an NBS Traceable NO Standard

Use the NBS traceable NO standard and the GPT calibration procedure to calibrate the NO, NOx and NO2 responses of a chemiluminescence analyzer. Refer to the GPT calibration procedure (4) for exact details; ignore the recommended zero offset adjustments. Generate several NO2 concentrations by dilution of the working NO2 standard to give on-scale NO2 responses. Measure the total flow at the manifold, Ft, for each NO2 concentration generated. Plot the analyzer NO2 response versus 1 F/T and determine the slope, SSTD. Calculate the permeation rate, R, from

$$R = \frac{SSTD}{K.} \qquad (14)$$

Intercomparison of NO2 and NO Working Standards

To compare the working NO2 standard to a certified NO working standard, simply **follow** the same procedure as outlined above for "certifying an NO2 working standard against an NB S traceable NO standard". The NO2 and NOX span adjustments must take into account: any N02 impurity in the NO working standard. To make comparison between a working NO standard and a certified NO2 standard,

follow the same procedure as outlined for "certifying a working NO standard against an NBS traceable NO2 standard". This procedure was discussed in the GPT section.

REFERENCES

1. Environmental Protection Agency, Title 40, Code of Federal Regulations, "Part 50 - National Primary and Secondary Ambient Air Quality Standards," Federal Register, 36, 8186, April 30, l 971

2. T. R. Hauser and C. M. Shy, Envir.Sci.Tech..6. 890 (1972).

3. Environmental Protection Agency, Title 40, Code of Federal Regulations, "Part 50 - Reference Method for Determination of Nitrogen Dioxide," Federal Register. 38. 15174, June 8, 1973.

4. Environmental Protection Agency, Title 40, Code of Federal Regulations, "Part 50 Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescence), "Federal register, 41. 52688, December 1, 1976.

5. Environmental Protection Agency, Title 40, Code of Federal Regulations, "Part 53 - Ambient Air Monitoring Reference and Equivalent Methods," Federal Register. 40 (33), 7044, February 18, 1975 as amended in Federal Register. 41, 5-2692, December 1, 1976.

6. E. C. Ellis and J. H. Margeson, 'Evaluation of Gas Phase Titration Technique as Used for Calibration of Nitrogen Dioxide Chemiluminescence Analyzers." Environmental Protection Agency, Research Triangle Park, NC, EPA Publication No. EPA-650/4-75-021, April 1975.

7. A. Fontijn, A. J. Sabadell, and R. J. Ronco, "Homogeneous Chemiluminescent Measurement of nitric Oxide with Ozone," Anal.Chem.,42, 575 (1970).

8. D. H. Stedman, E. E. Daby, F. Stuhl, and H., Niki, "Analysis of Ozone and Nitric oxide by a Chemiluminescent Method in Laboratory and Atmospheric Studies of Photochemical Smog," J.Air Poll. Control Assoc.. 22, 260 (1972).

9. B. E. Martin, J. A. Hodgeson and R. K. Stevens, "Detection of Nitric Oxide Chemiluminescence at Atmospheric Pressure," Presented at 164th National American Chemical Society Meeting, New York City, August 1972.

10. R . K. Stevens and J. A. Hodgeson, "application of Chemiluminescent Reactions to the Measurement of Air Pollutants, " Anal.Chem..45. 443A (1973).

11. J. A. Hodgeson, K. A. Rehme, B. E. Martin, and R. K. Stevens, "Measurement for Atmospheric Oxides of Nitrogen and Ammonia by Chemiluminescence," Preprint, presented at 1972 Air Pollution Control Association Meeting, Miami, Florida, June 1972, Paper No. 72-12.

12. L. P. Breitenbach and M. Shelef, "Development of a Method for the Analysis of NO2 and NH3 by NO-Measuring Instruments," J.Air Poll.Control Assoc..23, 128 (1973).

13. A.M. Winer, J. W. Peters, J. P. Smith and J. N. Pitts, Jr., "Response of Commercial

Chemiluminescent No-NO2 Analyzers to other Nitrogen-Containing Compounds," Envir.Sci.Tech..8. 1118 (1974).

14. P. C. Constant, M. C. Sharp and G. W. Scheil, "Collaborative Testing of Methods for Measurement of NO2 in Ambient Air," EPA Report No. 650/4-75-013, February 1975.

15. K. A. Rehme, B. E. Martin, and J. A. Hodgeson, "Tentative Method for the Calibration of Nitric Oxide, Nitrogen Dioxide and Ozone Analyzers by Gas Phase Titration," Environmental Protection Agency, Research Triangle Park7 NC, EPA Publication No. EPA-R2-73-246, March 1974.

16. M. A. A. Clyne, B. A. Thrush and R. P. Wayne, Trans.Faradav Soc.. 60, 359 (1964).

17. J. A. Hodgeson, R. K. Stevens, and B. E. Martin, "A Stable Ozone Source applicable as a Secondary standard for Calibration of Atmospheric Monitors," ISA Transactions.ll, 161 (1972).

18. NBS technical Note, No. 585, pp. 11-25 (January 1972). Available through: Superintendent of Documents, Government Printing Office, Washington, DC 20402. Price $.70.

19. G. O. Nelson, Controlled Test Atmospheres. (Ann Arbor Science Publishers, Inc., Ann Arbor, 1971), Chapter 3.

20. K. A. Rehme and C. F. Smith, Environmental Monitoring and Support Laboratory, Environmental Protection A~ency, private communication.

21. A. E. O'Keeffe and G. C. Ortman, "Primary Standards for Trace Gas Analysis." Anal., Chem.. 38. 760 (1966).

22. F. P. Scaringelli, A. E. O'Keeffe, E. Rosenberg, and J. B. Bell, "Preparation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically," Anal.Chem..42, 871 (1970).

23. H. L. Rook, E. E. Hughes, R. G. Fuerst and J. H. Margeson, Operation Characteristics of No2 Permeation Devices," Anal.chem. In Press.

24. Calibration in Air Monitoring. ASTM STP 598, (American society for Testing and Materials, Philadelphia, 1976).

ADDENDUM

Part 50 of chapter I, Title 40, Code of Federal Regulations, is amended by revising Appendix F to read as follows:

APPENDIX F - MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF NITROGEN DIOXIDE IN THE ATMOSPHERE (GAS PHASE CHEMILUMINESCENCE)

Principle and Applicability

1. Atmospheric concentrations of nitrogen dioxide (NO2) are measured indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nanometers, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (03). (1,2,3) NO2 is first quantitatively reduced to NO (4,5,6,) by means of a converter. NO, which commonly exist in ambient air together with NO2, passes through the converter unchanged causing a reusultant total NOX concentration equal to NO + NO2. -A sample of the input air is also measured without having passed through the converter. This latter NO measurement is subtracted from the former measurement (NO + NO2) to yield the final NO2 measurement. The NO and NO + NO2 measurements may be made concurrently with dual systems, or cyclically with the same system provided the cycle time does not exceed 1 minute.

2. Sampling considerations.

2.1 Chemiluminescence NO/NOX/NO2 analyzers will respond to other nitrogen containing compounds, such as peroxyacetyl nitrate (PAN), which might be reduced to NO in the thermal converter. (7) Atmospheric concentrations of thee potential interferences are generally low relative to NO2 and valid NO2 measurements may be obtained. In certain geographical areas, where the concentration of thee potential interferences is known or suspected to be high relative to N02, the use of an equivalent method for the measurement of NO2 is recommended.

2.2 The use of integrating flasks on the sample inlet line of chemiluminescence NO/NOX/NO2 analyzers is strongly discouraged. The sample residence time between the sampling point and the analyzer should be kept to a minimum to avoid erroneous NO2 measurements resulting from the reaction of ambient levels of NO and 03 in the sampling system.

2.3 The use of particulate filters on the sample inlet line of chemiluminescence NO/NOX/NO2 analyzers is optional and left to the discretion of the user or the manufacturer. Use of the filter should depend on the analyzer' susceptibility to interference, malfunction, or damage due to particulates. Users are cautioned that particulate matter concentrated on a filter may cause erroneous NO2 measurements and therefore filters should be changed frequently.

3. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Park 53 of this chapter.

Calibration

1. Alternative A - Gas phase titration (GPI) of an NO standard with 03.

Major Equipment Required: Stable 03 generator.
Chemiluminescence NO/NOX/NO2 analyzer with strip Chart recorder(s).
No concentration standard.

1.1 Principle. This calibration technique is based upon the rapid gas phase reaction between NO and 03 to produce stoichiometric quantities of NO2 in accordance with the following equation: (8)

NO+03--NO2+02 (1)

The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO2 can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO/NOX/NO2 analyzer is used as an indicator of changes in NO concentration. Upon the addition of 03, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO2 produced. The amount of NO2 generated may be varied by adding variable amounts of 03 from a stable uncalibrated 03 generator. (9)

1.2 Apparatus. Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the 03 generator should be of glass, Teflon, or other nonreactive material.

1.2.1 Air flow controllers. Devices capable of maintaining constant air flows within ±2% of the required flowrate.

1.2.2 No low controller. A device capable of maintaining constant NO flows within ± 2% of the required flowrate. Component parts in contact with the NO should be of a non-reactive materials.

1.2.3 Air flowmeters. Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of I 2% of the measured flowrate.

1.2.4 NO flowmeter. A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of +2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

1.2.5 Pressure regulator for standard NO cylinder. This regulator must have a non-reactive diaphragm and internal parts and a suitable delivery pressure.

1.2.6 Ozone generator. The generator must be capable of generating sufficient and stable levels of 03 for reaction with NO to generate NO2 concentrations in the range required. Ozone generators of the electric discharge type may produce NO and NO2 and are not recommended.

1.2.7 Valve. A valve may be used as shown in Figure 1 to divert the NO flow when zero air is required at the manifold. The valve should be constructed of glass, Teflon, or other nonreactive materials.

1.2.8 Reaction chamber. A chamber, constructed of glass, Teflon, or other non-reactive materials, for the quantitative reaction of 03 with excess NO. The chamber should be of sufficient volume (VRC) such that the residence time (tR) meets the requirements specified in 1.4. For practical reasons, tR should be less than 2 minutes.

1.2.9 Mixing chamber. A chamber constructed of glass, Teflon, or other non-reactive material and designed to provide thorough mixing of reaction products and diluent air. The residence time if not critical when the dynamic parameter specification given in 1.4 is met.

1.2.10 Output manifold. The output manifold should be constructed of glass, Teflon, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

1.3 Reagents

1.3.1 NO concentration standard. Cylinder containing 50 to 100 ppm in N2 with less than 1 ppm NO2. The cylinder must be traceable to a National Bureau of Standards NO in N2 Standard Reference Material (SRM 1629). Procedures for certifying the NO cylinder (working standard) against an NBS traceable NO or NO2 standard and for determining the amount of NO2 impurity are given in reference 13. The cylinder should be recertified on a regular basis as determined by the local quality control program.

1.3.2 Zero air. Air, free of contaminants which will cause a detectable response on the NO/NOX/NO2 analyzer or which might react with either NO, 03, or NO2 in the gas phase titration. A procedure for generating zero air is given in reference 13.

1.4 Dynamic parameter specification.

1.4.1 The 03 generator air flowrate (FO) and NO flowrate (FNO) (see Figure 1) must be adjusted such that the following relationship holds:

$$PR = [NO]RC \times tR \geq 2.75 \text{ ppm-minutes} \quad (2)$$

$$[NO]RC = [NO]STD \left(\frac{FNO}{FO + FNO}\right) \quad (3)$$

$$tR = \frac{VRC}{FO + FNO} < 2 \text{ minutes} \quad (4)$$

where: PR = dynamic parameter specification, determined empirically, to insure Complete reaction of the available 03, ppm-minute

[NO]RC = NO concentration in the reaction chamber, ppm

tR = residence time of the reactant gases in the reaction chamber, minute

[NO]STD = concentration of the undiluted NO standard, ppm

FNO = NO flowrate, scm3/min

FO = 03 generator air flowrate, scm3/min

VRC = volume of the reaction chamber, scm3

1.4.2 The flow conditions to be used in the GPI system are determined by the following procedure.

(a) Determine FT, the total flow required at the output manifold (FT = analyzer demand plus 10 to 50% excess).

(b) Establish [NO]OUT as the highest NO concentration (ppm) which will be required at the output manifold. [NO]OUT should be approximately equivalent to 90% of the upper range limit (URL) of the NO2 concentration range to be covered.

© Determine FNO as

$$FNO = \frac{[NO]OUT \times FT}{[NO]STD} \quad (5)$$

(d) Select a convenient or available reaction chamber volume. Initially, a trial VRC may be selected to be in the range of approximately 200 to 500 scm3.

(e) Compute FO as

$$FO = \frac{[NO]STD \times FNO \times VRC}{2.75} - FNO \quad (6)$$

(f) Compute tR as

$$tR = \frac{VRC}{FO + FNO} \quad (7)$$

Verify that tR < 2 minutes. If not, select a reaction chamber with a smaller VRC.

(g) Compute the diluent air flowrate as

$$FD = FT - FO - FNO \quad (8)$$

where: FD = diluent air flowrate, scm3/min

(h) If FO turns out to be impractical for the desired system, select a reaction chamber having a different VRC and recompute FO and FD.

NOTE: A dynamic parameter lower than 2.75 ppm-minutes may be used if it can be determined empirically that quantitative reaction of 03 with NO occurs. A procedure for making this determination as well as more detailed discussion of the above requirements and other related considerations is given in reference 13.

1.5 Procedure

1.5.1 Assemble a dynamic calibration system such as the one shown in Figure 1.

1.5.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soapbubble meter or wet-test meter. All volumetric flowrates should be corrected to25 degrees C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

1.5.3 Precautions must be taken to remove 02 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator ha been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

1.5.4 Select the operating range of the NO/NOX/NO2 analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NOx channels on higher ranges is desired, subsequent recalibration of the NO and NOX channels on the higher ranges is recommended.

NOTE: Some analyzer designs may require identical ranges for NO, NOX, and NO2 during operation of the analyzer.

1.5.5 Connect the recorder output cable(s) of the NO/NOX/NO2 analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

1.5.6 Determine the GPT flow conditions required to meet the dynamic parameter specification as indicated in 1.4.

1.5.7 Adjust the diluent air and 03 generator air flows to obtain the flows determined in 1.4.2. The total air flow to obtain the flows determined in 1.4.2. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until table NO,NOx, and N02 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE: Some analyzers may have separate zero controls for NO, NOX, and N02. Other analyzers may have separate zero controls only for NO and NOX, while still others may have only one zero control common to all three channels.

Offsetting the analyzer zero adjustments to +5% of scale is recommended to facilitate observing negative zero drift. Record the table zero air responses as ZNO,ZNOx, and ZN02.

1.5.8 Preparation of NO and N0x calibration curves.

1.5.8.1 Adjustment of NO span control. Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80% of the upper range limit (URL) of the NO range. The exact NO concentration is calculated from:

$$[NO]OUT = \frac{FNOx[NO]STD}{FNO+FO+FD} \quad (9)$$

where: [NO]OUT= diluted NO concentration at the output manifold, ppm.

Sample this NO concentration until the NO and NOX responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[NO]OUT}{URL} \times 100\right) + ZNO \quad (10)$$

where: URL = nominal upper range limit of the NO channel, ppm

NOTE: Some analyzers may have separate span controls for No,NOx, and N02. Other analyzes may have separate span controls only for NO and NOX, while still others may have only one span control common to all three channels., When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

If substantial adjustment of the No span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.1. Record the NO concentration and the analyzer's NO response.

1.5.8.2 Adjustment of NOX span control. When adjusting the analyzer NOX span control, the presence of any N02 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of N02 impurity in the standard NO cylinder are given in reference 13. The exact NOX concentration is calculated from:

$$[Nox]OUT = \frac{FNO \times ([NO]STD + [NO2]IMP)}{FNO + FO + FD} \quad (11)$$

where: [Nox]OUT = diluted NOx concentration at the output manifold, ppm

[NO2]IMP = concentration of NO2 impurity in the standard NO cylinder, ppm

Adjust the NOx span control to obtain a recorder response as indicated below:

$$\text{reorder response (\% scale)} = \left(\frac{[NOx]OUT}{URL} \times 100\right) + ZNOx \quad (12)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NOx.

If substantial adjustment of the NOx span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.8.2. Record the NOX concentration and the analyzer's NOX response.

1.5.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing FNO or increasing FD. For each concentration generated, calculate the exact NO and NOx concentrations using equations (9) and (11) respectively.

Record the analyzer's NO and NOX responses for each concentration. Plot the analyzer responses versus the respective calculated No and NOx concentrations and draw or calculate the No and NOx calibration curves. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero air point and NO and NOx concentrations of approximately 80% of the URL.

1.5.9 Preparation of NO2 calibration curve.

1.5.9.1 Assuming the NO2 zero has been properly adjusted while sampling zero air in step 1.5.7, adjust FO and FD as determined in 1.4.2. Adjust FNO to generate an NO concentration near 90% of the URL of the NO range. Sample this NO concentration until the NO and NOx responses have stabilized. Using the NO calibration curve obtained in 1.5.8, measure and record the NO concentration as [NO]orig.

1.5.9.2 Adjust the 03 generator to generate sufficient 03 to produce a decrease in the NO concentration equivalent to approximately 80% of the URL of the NO2 range. The decrease must not exceed 90% of the NO concentration determined in step 1.5.9.1. After the analyzer responses have

stabilized, record the resultant NO and NOx concentrations as [NO] rem and [Nox]rem.

1.5.9.3 Calculate the resulting NO2 concentration from:

$$[NO2]OUT = orig - [NO]rem + \frac{FNO \times [NO2]IMP}{NO + FO + FD} \quad (13)$$

where: [NO2]OUT = diluted NO2 concentration at the output manifold, ppm

[NO]orig = original NO concentration, prior to addition of 03, ppm

[NO]rem = NO concentration remaining after addition of 03, ppm

Adjust the NO2 span control to obtain a recorder response as indicated below:

$$\text{Recorder response (\% scale)} = \left(\frac{[NO2]OUT}{URL} \times 100\right) + ZNO2 \quad (14)$$

NOTE: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NOx channels and no further adjustment is made here for NO2.

If substantial adjustment of the NO2 span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 1.5.7 and 1.5.9.3. Record the NO2 concentration and the corresponding analyzer NO2 and NOx responses.

1.5.9.4 Maintaining the same FNO, FO, and FD as in 1.5.9.1, adjust the ozone generator to obtain several other concentrations of NO2 over the NO2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO2 concentration using equation (13) and record the corresponding analyzer NO2 and NOx responses. Plot the analyzer's NO2 responses versus the corresponding calculated NO2 concentrations and draw or calculate the NO2 calibration curve.

1.5.10 Determination of converter efficiency.

1.5.10.1 For each NO2 concentration generated during the preparation of the NO2 calibration curve (see 1.5.9) calculate the concentration of NO2 converted from:

$$[NO2]CONV = [NO2]OUT - ([Nox]orig - [Nox]rem) \quad (15)$$

where: [NO2]CONV = concentration of NO2 converted, ppm

[Nox]orig = original NOx concentration prior to addition of 03, ppm

[NOx] rem = NOx concentration remaining after addition of 03, ppm

Plot [NO2]CONV (y-axis) versus [NO2]OUT (x-axis) and draw or calculate the converter efficiency

curve. The slope of the curve times 100 is the average converter efficiency, EC. The average converter efficiency must be greater than 96%; if it is less than 96%, replace or service the converter.

NOTE: supplemental information on calibration and other procedures in this method are given in reference 13.

2. Alternative B - NO2 permeation device.

Major equipment required: Stable 03 generator.
Chemiluminescence NO/NOX/NO2 analyzer
with strip chart recorder(s).
NO concentration standard.
NO2 concentration standard.

2.1 Principle. Atmospheres containing accurately known concentrations of nitrogen dioxide are generated by means of a permeation device. (10) The permeation device emits NO2 at a known constant rate provided the temperature of the device is held constant (±0.1 degrees C) and the device has been accurately calibrated at the temperature of use. The NO2 emitted from the device is diluted with zero air to produce NO2 concentrations suitable for calibration of the NO2 channel of the NO/NOX/NO2 analyzer. An NO concentration standard is used for calibration of the NO and NOx channels of the analyzer.

2.2 apparatus. A typical system suitable for generating the required NO and NO2 concentrations is shown in Figure 2. All connections between components downstream from the permeation device should be of glass, Teflon, or other non0reactive material.

2.2.1 Air flow controllers. Devices capable of maintaining constant air flows within ±2% of the required flowrate.

2.2.2 NO flow controller. A device capable of maintaining constant No flows within ±2% of the required flowrate. Component parts in contact with the No must be of a non-reactive material.

2.2.3 Air flowmeters. Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

2.2.4 NO flowmeter. A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.2.5 Pressure regulator for standard NO cylinder. This regulator must have a non-reactive diaphragm and internal parts and a suitable delivery pressure.

2.2.6 Drier. Scrubber to remove moisture from the permeation device air stream. The use of the drier is optional with NO2 permeation devices not sensitive to moisture. (Refer to the supplier's instructions for use of the permeation device.)

2.2.7 Constant temperature chamber. Chamber capable of housing the NO2 permeation device and maintaining its temperature to within ±0.1 degrees C.

2.2.8 Temperature measuring device. Device capable of measuring and monitoring the temperature of the NO2 permeation device with an accuracy of ±0.05 degrees C.

2.2.9 Valves. A valve may be used as shown in Figure 2 to divert the NO2 from the permeation device when zero air or NO is required at the manifold. A second valve may be used to divert the NO flow when zero air or NO2 is required at the manifold. The valves should be constructed of glass, Teflon, or other nonreactive material.

2.2.10 Mixing chamber. A chamber constructed of glass, Teflon, or other non-reactive material and designed to provide thorough mixing of pollutant gas streams and diluent air.

2.2.11 Output manifold. The output manifold should be constructed of glass, Teflon, or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.3 Reagents.

2.3.1 Calibration standards. Calibration standards are required for both NO and NO2. The reference standard for the calibration may be either an NO or NO2 standard. The reference standard must be used to certify the other standard to ensure consistency between the two standards.

2.3.1.1 NO2 concentration standard. A permeation device suitable for generating NO2 concentrations at the required flowrates over the required concentration range. If the permeation device is used as the reference standard, it must be traceable to a National Bureau of standards NO2 Standard Reference Material (SRM 1629) or NO in N2 Standard Reference Material (SRM 1683 or SRM 1684). If an NO cylinder is used as the reference standard, the NO2 permeation device must be certified against the NO standard according to the procedure given in reference 13. The use of the permeation device should be in strict accordance with the instructions supplied with the device. Additional information regarding the use of permeation devices is given by Scaringelli et al. (11) and rook et al. (12)

2.3.1.2 NO concentration standard. Cylinder containing 50 to 100 ppm NO in N2 with less than 1 ppm NO2. If the cylinder is used as the reference standard, it must be traceable to a National Bureau of Standards NO in N2 Standard Reference Material (SRM 1683 or SRM 1684) or NO2 Standard Reference Material (SRM 1629). If an NO2 permeation device is used as the reference standard. The NO cylinder must be certified against the NO2 standard according to the procedure given in reference 13. The cylinder should be recertified on a regular basis as determined by the local quality control program. A procedure for determining the among of NO2 impurity in the No cylinder is also given in reference 13.

2.3.3 Zero air. Air, free of contaminants which might react with NO or NO2 or cause a detectable response on the NO/NO/NO2 analyzer. When using permeation devices that are sensitive to moisture, the zero air passing across the permeation device must be dry to avoid surface reactions on the

device. (Refer to the supplier's instructions for use of the permeation device.). A procedure for generating zero air is given in reference 13.

2.4 Procedure.

2.4.1 Assemble the calibration apparatus such as the typical one shown in Figure 2.

2.4.2 Insure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter. All volumetric flowrates should be corrected to 25 degrees C and 760 mm Hg. A discussion on the calibration of flowmeters is given in reference 13.

2.4.3 Install the permeation device in the constant temperature chamber. Provide a small fixed air flow (200-400 scm3/min) across the device. The permeation device should always have a continuous air flow across it to prevent large buildup of NO2 in the system and a consequent restabilization period. Record the flowrate as FP. Allow the device to stabilize at the calibration temperature for at least 24 hours. The temperature must be adjusted and controlled to within $\pm$0.1 degrees C or less of the calibration temperature as monitored with the temperature measuring device.

2.4.4 Precautions must be taken to remove 02 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in reference 13.

2.4.5 Select the operating range of the NO/NOX/NO2 analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO2 calibration, all three channels of the analyzer should be set to the same range. If operation of the NO and NOx channels on higher ranges is desired, subsequent recalibration of the No and NOx channels on the higher ranges is recommended.

NOTE: Some analyzer designs may require identical ranges for NO, NOx, and NO2 during operation of the analyzer.

2.4.6 connect the recorder output cable(s) of the NO/NOX/NO2 analyzer to the input terminals of the strip chart recorder(s). All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

2.4.7 Switch the valve to vent the flow from the permeation device and adjust the diluent air flowrate, FD, to provide zero air at the output manifold. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NOx, and NO2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s).

NOTE: some analyzers may have separate zero controls for NO, NOx, and NO2. Other analyzers may have separate zero controls only for NO and NOx, while still others may have only one zero control common to all three channels.

Offsetting the analyzer zero adjustments to +5% of scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as ZNO, ZNOx, and ZNO2.

2.4.8 Preparation of NO and NOx calibration curves.

2.4.8.1 Adjustment of NO span control. Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80% of the upper range limit (URL) of the NO range. The exact NO concentration is calculated from:

$$[NO]OUT = \frac{FNO \times [NO]STD}{FNO + FD} \quad (16)$$

where: [NO]OUT = diluted NO concentration at the output manifold, ppm

FNO = NO flowrate, scm3/min

[NO]STD = concentration of the undiluted NO standard, ppm

FD = diluent air flowrate, scm3/min

Sample this NO concentration until the No and NOx responses have stabilized. Adjust the No span control to obtain a recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[NO]OUT}{URL} \times 100\right) + ZNO \quad (17)$$

where: URL = nominal upper range limit of the NO channel, ppm

NOTE: some analyzers may have separate span controls for NO, NOx, and NO2. Other analyzers may have separate span controls only for NO and NOX, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made o the NO channel of the analyzer.

If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps, 2.4.7 and 2.4.8.1. Record the No concentration and the analyzer's NO response.

2.4.8.2 Adjustment of NOx span control. When adjusting the analyzer's NOx span control, the presence of any NO2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO2 impurity in the standard NO cylinder must be taken into account. Procedures for determining the amount of NO2 impurity in the standard NO cylinder are given in reference

13. The exact NOx concentration is calculated from:

$$[Nox]OUT = \frac{FNO \times ([NO]STD + [NO2]IMP)}{FNO + FD} \quad (18)$$

where: [Nox]OUT = diluted NOx concentration at the output manifold, ppm

[NO2]IMP = concentration of NO2 impurity in the standard NO cylinder, Ppm

Adjust the NOx span control to obtain a convenient recorder response as indicated below:

$$\text{Recorder response (\% scale)} = \left(\frac{[Nox]OUT}{URL} \times 100\right) + ZNOx \quad (19)$$

NOTE: If the analyzer has only one span control, the span adjustment is made on the NO channel and no further adjustment is made here for NOx.

If substantial adjustment of the NOx span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.8.2. Record the NOx concentration and the analyzer's NOx response.

2.4.8.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing FNO or increasing FD. For each concentration generated, calculate the exact NO and NOx concentrations using equations (16) and (18) respectively. Record the analyzer's No and NOx responses for each concentration. Plot the analyzer responses versus the respective calculated NO and NOx concentrations and draw or calculate the NO and NOx calibration curves. For subsequent calibrations where Linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero air point and NO and NOx concentrations of approximately 80% of the URL.

2.4.9 Preparation of NO2 calibration curve.

2.4.9.1 Remove the NO flow. Assuming the NO2 zero has been properly adjusted while sampling zero air in step 2.4.7, switch the valve to provide NO2 at the output manifold.

2.4.9.2 Adjust FD to generate and NO2 concentration of approximately 80% of the URL of the NO2 range. The total air flow must exceed the demand of the analyzer(s) under calibration. The actual concentration of NO2 is calculated from:

$$[NO2]OUT = \frac{R \times K}{FP + FD} \quad (20)$$

where: [NO2]OUT = diluted NO2 concentration at the output manifold, ppm

R = permeation rate, ug/min

K = 0.532 ul NO2/ug NO2 (at 25 degrees C and 760 mm Hg)

FP = air flowrate across permeation device, scm3/min

FD = diluent air flowrate, scm3/min

Sample this NO2 concentration until the NOx and NO2 responses have stabilized. Adjust the NO2 span control to obtain a recorder response as indicated below:

$$\text{Recorder response (\% scale)} = \left(\frac{[NO]OUT}{URL} \times 100\right) + ZNO2 \qquad (21)$$

NOTE: If the analyzer has only one or two span controls, the plan adjustments are made on the No channel or NO and NOx channels and no further adjustment is made here for NO2.

If substantial adjustment of the NO2 span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps 2.4.7 and 2.4.9.2. Record the NO2 concentration and the analyzer's NO2 response. Using the NOx calibration curve obtained in step 2.4.8, measure and record the NOx concentration as [Nox]M.

2.4.9.3 Adjust FD to obtain several other concentrations of NO2 over the NO2 range (at least five evenly spaced points across the remaining scale are suggested.) Calculate each NO2 concentrations and draw or calculate the NO2 calibration curve.

2.4.10 Determination of converter efficiency.

2.4.10.1 Plot [Nox]M (y-axis) versus [NO2]OUT (x-axis) and draw or calculate the converter efficiency curve. The slope of the curve times 100 is the average converter efficiency, EC. The average converter efficiency must be greater than 96%; if it is less than 96%, replace or service the converter.

NOTE: supplemental information on calibration and other procedures in this method are given in reference 13.

3. Frequency of calibration. The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checks, will vary from one analyzer to another. The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent alteration as operational experience is accumulated. Manufacturers of analyzers should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, and quality control.

References

1. A. Fontijn, A. J. Sabadell, and r. J. Ronco, “Homogeneous chemiluminescent Measurement of Nitric Oxide with Ozone,” Anal. Chem., 42, 575 (1970)

2. D. H. Stedman, E. E. Daby, F. Stuhl, and H. Niki, “Analysis of Ozone and Nitric oxide by a Chemiluminescent Method in Laboratory and Atmospheric Studies of Photochemical Smog,” J.Air Poll. Control Assoc., 22 , 260 (1972).

3. B. E. Martin, J. A. Hodgeson, and R. K. Stevens, “Detection of Nitric oxide Chemiluminescence at Atmospheric pressure,” Presented at 164th National ACS Meeting, new York city, August 1972.

4. J. A. Hodgeson, K. A. Rehme, B. E. Martin, and R. K. Stevens, “Measurements for atmospheric oxides of Nitrogen and ammonia by chemiluminescence,” Presented at 1972, APCA meeting, Miami, Florida, June 1972.

5. R. K. Stevens and J. A. Hodgeson, “applications of Chemiluminescence Reactions to the Measurement of air Pollutants,” Anal. Chem., 45, 443A (1973).

6. L. P. Breitenbach and M. Shelef, “Development of a Method for the Analysis of NO2 and NH3 by NO-Measuring Instruments,” J. Air Poll. Control Assoc., 23, 128 (1973).

7. A. M. Winer, J. W. Peters, J. P. Smith, and J. N. Pitts, Jr., “Response of commercial Chemiluminescent No-NO2 Analyzers to Other Nitrogen-Containing compounds, “Environ.Sci.Techno., 8,1118 (1974).

8. K. A. Rehme, B. E. Martin, and J. A. Hodgeson, “Tentative Method for the Calibration of nitric Oxide, Nitrogen Dioxide, and Ozone Analyzers by Gas Phase Titration,” EPA-R2-73-246, March 1974.

9. J. A. Hodgeson, R. K. Stevens, and B. E. Martin, “A Stable Ozone source applicable as a Secondary Standard for Calibration of Atmospheric Monitors,” ISA Transactions, 11, 161 (1972).

10. A. E. O’Keeffe and G. C. Ortman, ‘Primary standards for Trace Gas Analysis,” Anal.Chem., 38, 760 (1966).

11. F. P. Scaringelli, a. E. O’Keeffe, e. Rosenberg, and J. P. Bell, “Preparation of Known concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically,” Anal. Chem., 42, 871 (1970)

12. H. L. Rook, E. E. Hughes, R. S. Fuerst, and J. H. Margeson, “Operation Characteristics of NO2 Permeation Devices,” Presented at 167th National ACS Meeting, Los Angeles, California, April 1974.

13. E. C. Ellis, “Technical Assistance document for the chemiluminescence Measurement of Nitrogen dioxide,” EPA-E600/4-75-003 (Available in draft form from the United States Environmental Protection Agency, Department E (MD-76), Environmental monitoring and support Laboratory, Research Triangle Park, North Carolina 27711).
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FIGURES 1 AND 2 COULD NOT BE SCANNED INTO THIS DOCUMENT.

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3. Author: Elizabeth Carol Ellis, Ph.D

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8. ABSTRACT:

   Gas phase chemiluminescence has been designated as the reference measurement principle for the measurement of nitrogen dioxide (NO2) in the ambient atmosphere. Continuous analyzers based on this measurement principle may be calibrated with NO2 either from the gas phase titration of nitric oxide (NO) with ozone (03) or from an NO2 permeation device. This document presents pertinent technical information to aid in the understanding of the measurement principle and the prescribed calibration procedures and also includes illustrative examples on how to implement the calibration procedures. The discussion includes recommendations on how to recognize and eliminate potential errors in the individual calibration procedures as well as with the use of NO2 chemiluminescence analyzers. Suggestions on the design and construction of calibration apparatus and procedures for handling and certifying both NO and NO2 calibration standards are included also.

9. Key Words and Document Analysis

Nitrogen Dioxide	Chemiluminescence
Calibration	Air Pollution

10. Identifiers/Open Ended Terms

    NO2 Measurement
    NO2 Calibration
    Gas Phase titration
    NO2 Permeation Device

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